In What Form is Lime Present in Portland Cement

by Claude W. Wright

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Submitted to the School of Engineering of the University of Kansas for completion of Masters of Cheimcal Engineering.

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A Dissertation Presented to the Faculty

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PREFACE.

The object of this work is to bring together some of the facts and theories concerning lime in Portland Cement and to try to arrive at some conclusion as to its nature, cause, and manner of occurrence. I shall deal exclusively with Portland Cement because of its extensive use and great commercial value.

This work is being carried on in connection with the fellowship work in cement established at the University of Kansas by the Ash Grove Portland Cement Co. I wish to thank Mr. J. F. Mackey, the holder of this fellowship, for many valuable suggestions and other assistance.

University of Kansas.

March 1st, 1910.

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In What Form is Lime Present in Portland Cement?

In the manufacture of Portland Cement an intimate mixture of finely divided calcareous and argillaceous materials is heated between certain limits of temperature (1450 C - 1600 C.) in a kiln revolving at a definite rate. A definite quantity of argillaceous material which has, by experience been shown to give a sound clinker is used. But of what happens to these materials from the time they enter the kiln until they leave it, we know but little.

This much, however, we do know. The temperature of the kiln is sufficient to decompose both the argillaceous and calcareous materials. And that these products of decomposition of the raw materials combine to form other compounds is evident from an examination of the finished product. But what these compounds are, has been a matter of considerable disagreement among investigators.

Now ordinary Portland cement may be said to have this composition, - SiO_2 - 23%; Al_2O_3 - 7.50%; Fe_2O_3 -3.5% CaO - 63%; MgO - 1 %; SO_3 - 1.5%. There are, therefore, many possibilities for the formation of different compounds in Portland Cement. Silica forms compounds with alumina, ferric oxide, lime, and magnesia. Lime not only forms silicates but combines to form ferrites with the iron oxide and aluminates with the alumina. Many investigators have

sought to prepare some of these compounds and study their properties in an attempt to explain the cause of the hydraulic properties of Portland cement. Other investigators have examined the clinker with the petrographic microscope. Some have attempted to work out its constitution wholly from the results of a chemical analysis. And yet another class have sought to demonstrate their theories of the constitution of Portland cement by a study of the products obtained by the decomposition of Portland cement by various reagents, such as water, and lime water. But it is only within recent years that any systematic attempt has been made to clear up the problem.

Smeaton, an English engineer first questioned the constitution of cement. In 1756 he pointed out that clay was present in the limestone furnishing hydraulic lime.

Bergman, a Swedish scientist, a few years later detected a small amount of manganese in the limestone of Lena, attributed to this element the hydraulic properties of the lime prepared from it.

Guyton de Morreau, analyzed the principle hydraulic limes of France and found only one to contain manganese but affirms on his faith in Bergman that manganese is the cause of the hydraulicity of lime.

Laussure, (Voyages dans les Alpes, 3,192), made a similar investigation of the limes of Switzerland and did

not find them manganiferous. He, however, states that he believes in Bergman's idea. He adds that clay might replace manganese although it was inferior to it.

Callet Descotils, (Am. des Mines (1813), 34, 308), of the Ecoles des Mines, Paris, noticed that silica in hydraulic limes was soluble in acid, while that in limestone was not, which seemed to him to show that in the burning there was a combination of lime and silica.

Jicat, (Recherches experimentales sur les Martiers, 1818), a few years later published his first memoir on hydraulic limes. He demonstrated that by burning a mixture of lime and clay an artificial hydraulic product could be obtained, and demolished the theories in regard to the action of manganese. He showed also that silica was chiefly responsible for the hardening of mortars.

Berthier, (Arm. des Mines (1822), 1, 8, 483), confirmed, a short time after the conclusion of Jirat, and endeavored to determine the composition of the silicate of lime produced in the burning, in the laboratory, of a mixture of silica and lime by separating the free from the combined lime by means of the solubility of the former in water.

Rivot, (Arm. des Mines (1856) 5, 9, 505), the successor of Berthier at the Ecole des Mines, made extended

researches on the same subject and came to the conclusion that during the burning of a cement two substances were formed, SiO_3, $3CaO$ and $Al_2O_3.3CaO$, and that setting as with plaster, was due to simply hydration.

Fremy, Comptes rendus (1865) 60, 993, endeavored to confirm Rivot's theory by analytical methods. He failed to produce a silicate that would set with water but succeeded with the aluminate, and was led to attribute the hardening of mortars to the influence of the aluminate. His theory was contested strongly, as many hydraulic limes contained less than 2 per cent of alumina.

Laudrin (Comptes rendus, 96, 156 and 1229, 98, 1053) in 1883-4, proposed in one year three theories, one that clay acted according to Saussure's ideas; second, that a supposed silicate of lime, $3\ SiO_2.4CaO$ caused the setting by hydration, while the third involved the action of carbonic acid.

Merceron (association francaise Grenoble, 1885) proposed a theory which attributed setting to the dessication of the clay under the influence of heat disengaged in the hydration of the lime.

According to Le Chatelier the above were the only facts which investigators previous to his time have advanced to explain the constitution and setting of Portland cement.

The investigations of Le Chatelier into the properties of Portland Cement were the most comprehensive of any that had been carried on up to 1887. His work may be divided into three parts. The first part consisted in an attempt to prepare synthetically various compounds of lime, silica, alumina and iron oxide. The second part consisted of a complete examination under the polarizing microscope of Portland cement clinker and of its synthetic products prepared by him. The third part concerned the cause of the hydraulic properties of cement.

Le Chatelier prepared by heating to a high temperature a mixture of silica and lime, two calcium silicates.

Calcium Monosilicate, - $CaO.SiO_2$, - the commonly occurring mineral Wollastinite, - is crystalline, shows strong double refraction when viewed in one direction in polarizing light and very feeble double refraction in the other direction. It is not acted upon by pure water, solution of ammonium salts, or lime-water; sets to a hard mass in water saturated with carbon dioxide.

Di-Calcium Silicate, - $2CaO.SiO_2$, - compact, hard mass when taken hot from the crucible and let cool; but dusts if left cool in the crucible, forming prismatic fragments with feeble double refraction. It is decomposed by solutions of ammonium salts; but is quite stable in

the presence of either hot or cold water; sets to a hard mass in carbon dioxide water more rapidly than the monosilicate.

Le Chatelier was not successful in his attempts to form tri-calcium silicate, - $3CaO.SiO_2$, directly by heating the proper proportions of lime and silica. If, however, a flux of calcium chloride is used and the resulting chloro-silicate decomposed by steam at 450° C, a compound of the formulae 3 $CaO.SiO_2$ is obtained. It is volume constant and sets very slowly.

Of the hydrated calcium silicates, Le Chatelier prepared but one, - $CaO.SiO_2.5H_2O$. This compound, which he was unable to obtain by treating calcium silicate with water, was prepared by adding an excess of lime water to colloidal silica, or by the action of a salt of lime on an alkaline silicate, i.e., calcium chloride on sodium silicate.

Le Chatelier describes four compounds of lime and alumina obtained by fusing lime and alumina in the proper proportions.

Monocalcium Aluminate. - $CaO.Al_2O_3$, - difficulty fusible , when powdered it sets rapidly in water, - when treated with water it undergoes a partial decomposition, lime and alumina going into solution.

Di-calcium aluminate - 2 CaO.Al_2O_3 - a vitreous mass obtained together with 2 Al_2O_3.3CaO when two gram molecular weights of Alumina are fused with three of lime.

Tri-calcium aluminate - 3CaO.Al_2O_3 - crystalline, singly refractive, most easily fusible of the aluminates,

Tri-calcium di-aluminate - ortho-rhombic crystals of strong double refraction : sets hard in water, but is decomposed in water at 100° C : lime and alumina in varying amounts dissolve when it is treated with water.

There is, according to Le Chatelier, but one definite hydrated compound of lime and alumina produced by saturating with lime-water anhydrous aluminates. Its composition is represented by the formula Al_2O_3.4CaO.12H_2O.

Le Chatelier describes a fusible silico aluminate in which Fe_2O_3 replaces a part of the Al_2O_3 in $2SiO_2.Al_2O_3$. 3CaO. This compound is identical with the compound which forms the essential element in crystallized blast furnace slag. It is completely inert under the action of water.

Thin sections of clinker of the above compounds, and set cement were examined by Lc Chatelier with a petrographic microscope. The results of the examination of these synthetic products have already been described. His work on the examination of clinker opened up a very interesting and instructive field for original work. In Portland cement clinker he observed four materials :

1. The most prominent material was colorless, crystalline, pseudo-cubic, and of feeble double refraction, decomposed rapidly by ammonical salts: plays an important role during hardening: probably $3CaO.SiO_2$.

2. A dark but variable in color magma with stronger double refraction than 1., slowly decomposed by commercial salts; probably silico-alumina ferrite of lime.

3. Accesory constituents, variable in different samples.

a. Crystalline, translucent or opaque sections of a light yellowish color, with fine striations at 60° to each other - present in most cements; slowly decomposed by ammonical salts; not found in high limed cements; increases with silica and are connected with phenomena of dusting.

b. Very small crystals with high double refraction, slowly decomposed by ammonical salts.

c. Inactive zones, - slowly decomposed by ammonical salts.

Le Chatelier maintained that free-lime was not present in a good cement, because he found that the addition of even one per cent of calcium oxide diminishes the strength of the cement and at the same time prevents it from being volume constant. In set cement the only constituents present are $SiO_2.4CaO.2.5H_2O$, $Ca(Oh)_2$, and pro-

bably $Al_2O_3.4CaO,12H_2O$. Iron plays no part in the setting of cement. The first phenomenon to occur during the setting is the separation of crystals of $Ca(OH)_2$ and later the hydrated calcium silicate, and finally the aluminate. Le Chatelir was, however, not sure that the aluminate was actually present.

His equations to determine the quantity of lime which should be present in a good clinker are as follows:

CaO/SiO_2-Al_2O_3-Fe_2O_3 greater than 3, preferably 3.5 to 4.

CaO/SiO_2 + Al_2O_3 less than 3, preferably 2.5 to 2.7.

In these equations equivalents and not precentages of the various substances are used.

Work of Newkerry's: J.S. C.I. 1897, 16,,887-894.

By heating various quantities of lime with silica, (paper by Newkerry & Meyer, Com. & Eng.News, Nov. 1902) four silicates of lime were obtained without difficulty.

Di-calcium Silicate - $2CaO-SiO_2$, crystalline, translucent, dusts on cooling; if suddenly cooled by immersing in water dusting was prevented. The material which was suddenly cooled after drying and grinding yielded a white powder, sets slowly, and becomes quite hard at the end of one day. A pat remained very hard, on glass, at seven days Hot test - sound.

2-1/2 $CaO.SiO_2$, white clinker - does not dust - sets very slowly - fairly hard at seven days, and quite hard after six weeks; after setting one day a pat placed in steam hardened well: on glass after six hours - hard, sound.

Tri-calcium Silicate. $3CaO.SiO_2$ - white porous clinker does not dust; no heating when mixed with water; at end of 7 days pat was still rather soft; but was quite hard after six weeks; hot test - sound; on glass - hard;.

3-1/2 $CaO.SiO_2$, soft clinker - no dusting, pat, though hard, curved slightly from the glass, and cracked before placing in water; was very hard after six weeks. Hot test - sound; on glass - hard.

They formed three calcium silicates by heating together properly proportioned mixtures of pure lime and alumina.

Di-calcium aluminate, - $2CaO.Al_2O_3$,- white in powder form. - Sets in hot water very rapidly; pat, hard, and hard on glass after six weeks; fairly hard, tho soft inside, on glass, in hot test.

2-1/2 $CaO.Al_2O_3$ - on addition of water gives strong heating. - sets quickly; pat left glass in one day, had curved and cracked in three days, and was still soft at six weeks. Hot test - soft, curved, cracked.

Tri-calcium Aluminate - heats strongly with water;

sets rapidly; pat, curved, cracked before putting in water and disintegrated entirely in water; hot test - curved, cracked, soft. By heating the proper quantities of lime and iron oxide, the compound $2CaO.Fe_2O_3$ was formed.

Di-calcium ferrite. , fuses readily to a black slag; powder - brown; does not heat with water; does not set or harden in air or water; in steam, after one day in air, a pat hardening rapidly and was quite sound and very hard after several hours.

They also prepared three compounds of magnesia and alumina; - Magnesium aluminate - $MgO.Al_2O_3$; di-magnesium aluminates, - $2MgO.Al_2O_3$, tri-magnesium aluminate, $3MgO.Al_2O_3$. These materials showed no signs of fusion or sintering, and were light porous and soft. The pulverized materials gave no indication of setting, and after standing several days in moist air, completely disintegrated when placed in water. Pats of these materials will not harden in steam. Three compounds of magnesia and silica were prepared.

Mono-magnesium silicate, - $MgO.SiO_2$, hard clinker; does not set in air, water or steam.

Di-magnesium silicate, - hard, porous clinker; has no setting properties.

Tri-magnesium silicate - $3MgO.SiO_2$ - infusible; porous, soft clinker; does not harden in water or steam.

The results led the Newkerrys to conclude that in the hardening of cement probably no part is played by the magnesia compounds.

It may be seen from these results that the most basic compounds of lime and silica and lime and alumina which have good hydraulic properties are tri-calcium silicate, and di-calcium aluminate. This being the case, the Newberrys gave the following formula for a sound portland cement:-

$$x(3CaO.SiO_2) + y(2CaO.Al_2O_3)$$

or substituting weights for equivalents,

$$\% CaO = \%SiO_2 \times 2.8 + \% Al_2O_3 \times 1.1$$

Many cements made from this formula gave satisfactory results up to an alumina content of 12 per cent, which produced a quick-setting cement of low tensile strength. They found that cements in which Fe_2O_3 replaced considerable Al_2O_3 were quite sound.

Depending on the method of formation Newkerry & Meyer prepared two kinds of tri-calcium silicates:-

1. When calcined at white heat, product is volume constant, free from uncombined lime and silica S.G. 3.055; has not perfect hardening properties; on suspending in sufficient water to dissolve the lime, $3CaO.2SiO_2,3H_2O$ is obtained.

2. When fused in Oxy-hydrogen flame - doubly refractive, rectangular cleavage ; S. G. 3.022; perfect hardening properties; on suspending in sufficient water to dissolve the lime, 2 CaO.SiO_2.H_2O is obtained.

When 2 CaO.SiO_2 which had dusted on suspending i n water was but slightly hydrated.

Various other hydrated silicates were obtained.

In an article in Thonindustrie-Zeitung, 1897, A. E. Törnekorm, gave the results of a very important investigation carried out by him on portland cement clinker. The work was undertaken without the knowledge of Le Chatelier's work and confirmed the latter's work on the optical properties of the constituents of portland cement clinker. These were five in number, Alite, Belite, Celit Felit and an isotropic mass. They correspond to No. I, 3(a), 2, 3b, and 3c of Le Chatelier's constituents. High limed cements consist almost entirely of alit and celit. Törnekorm considers alit as a compound of silica, alumina and lime primarily.

In the Chem. Ind. 1898, 21, 69 and 96, Karl Zulkowski considers that lime in Portland cement is the dicalcium silicate SiO_2.2CaO, because he was unable to prepare the tri-calcium silicate. He admits that free lime must be present and explains that its being hard burned prevents it from blowing. The possibility of a

solution of lime and a saturated silica magma he considers not to be out of the question.

In 1898 Rebuffat conducted a series of experiments to determine the action of sugar solutions upon hydraulic limes and on quick and slow setting cements. These experiments were intended to show the different states of combination of the lime in the cement from the amount found to be soluble and insoluble in the sugar solution. He also prepared and described various aluminates and silicates. He was unable to obtain $SiO_2.3CaO$.

In his conclusions Rebuffat does not consider it of importance whether alit consists of pure $SiO_2.3CaO$ or a crystalline compound of $SiO2.2CaO$ with CaO and an aluminate. He says the aluminate in Portland Cement cannot be $Al_2O_3.3CaO$. Even with 64% of lime, this is not sufficient to combine with all the silica as $SiO_2.3CaO$ and at the same time with Al_2O_3 as $Al_2O_3.3CaO$.

In 1901, A. Meyer, A Romanian Engineer, published (Bull. d. Soc. Des Sciences de Boucarest 9 No. 6) the most valuable resumé of the literature on the subject of the the constitution of Portland cement which had appeared up to that time, and has discussed the entire evidence which is available.

Meyer insists that free lime cannot exist in a well burned cement for three reasons: 1. The addition of

of as little as 1 per cent of freshly burned lime to a normal cement is enough to destroy its stability. 2. An excess of carbonate of lime in the raw mixture, even if a very small one causes like appearances, and 3. A cement of medium lime contents if not well ground and uniformly mixed, or if not well burned is unstable in water.

Meyer's conclusions are not founded on his own work, but are derived from the experiments of others, and from the evidence afforded by peculiarities developed in the production of various kinds of clinker. His conclusions that have a direct bearing on free lime are as follows

(1) Cement is a body composed of a greater or less number of minerals which vary according to the bacisity and method of burning the cement. Two of these minerals form the essential constituents of the cement. They are the tri-calcium silicate and the magma or flux whose composition is changeable. The other minerals, three in number, vary in different cements and can be entirely wanting. These minerals are (1) an isomorphous mixture of tri-calcium and dicalcium silicates; (2) a calcium silico aluminate which is chiefly found in underburned cements.

(2) The largest possible amount of lime which can exist in cement is that which, after the formation of tri-calcium silicate, will form a multiple iron alumina, lime silicate of the extreme saturation represented by the for-

mula, - $X(SiO_2.3CaO) + Y(SiO_2R_2O_3.6CaO)$. This formula can be worked out for each special case, in that the maximum quantity of lime shall not exceed that expressed by the relation $MO.-6R_2O_3/SiO_2-R_2O_3$ less than 3., where M = Ca, Mg, Na and K, and R = Al, Fe and Mn.

The work of Clifford Richardson on the constitution of Portland Cement is probably the most exhaustive and thorough of any work along this line. In 1905 as a result of exhaustive microscopic study of Portland Cement Clinker the preparation of many synthetic silicates and aluminates, he advanced the theory that Portland cement clinker is a solid solution. The silicates and aluminates that he prepared may be described as follows:

Mono-calcic silicate , - $SiO_2.CaO$: A crystalline substance of high optical activity and little hydraulic properties.

Di-calcic silicate, $SiO_2.2CaO$: A definite crystalline compound of high optical activity and little hydraulic activity.

Tri-calcic silicate, $SiO_2.3CaO$: A definite crystalline silicate of low optical activity. Its hydraulic activity is greater than that of di-calcic silicate. If fused and reground it sets slowly like Portland cement.

Mono-calcic aluminate, - $Al_2O_3.CaO$: A crystalline substance of high optical activity but not sufficiently

basic to be found in a material of such basic character as Portland cement.

Tri-calcic di-aluminate, $2Al_2O_3.3CaO$: An aluminate of highly crystalline character and of great optical activity.

Di-calcic aluminate, $Al_2O_3.2CaO$: A substance crystallizing from a state of fusion in dendritic forms, having no optical activity and being therefore, isotropic.

Tri-calcic aluminate, $Al_2O_3.3CaO$. This aluminate crystallizes from the fused condition in elongated octahedra. It is isotropic and is undoubtedly a definate silicate.

Richardson says that alit is a solid solution of tri-calcic silicate in tri-calcic aluminate. He says it may be readily seen that the di-calcic aluminate could not become dissolved in tri-calcic aluminate without reaction going on and an interchange of base between the tri-calcic silicate and di-calcic aluminate to such an extent as to convert a portion of the di-calcic aluminate to the tri-calcic form and a corresponding portion of the tri-calcic silicate to the di-calcic form. The tri-calcic aluminate then dissolves in the tri-calcic silicate and the di-calcic aluminate in the di-calcic silicate thus forming two separate and distinct solid solutions, the one alit and the other celit, which are not miscible in the solid form.

Richardson also concludes that the setting of Portland cement is almost entirely due to the decomposition of the alit, examination showing celit to be almost unattached; and that the strength of Portland cement after setting is due entirely to the crystallization of calcium hydrate, and not at all to the hydration of the silicates and aluminates. His theory is that "on addition of water to the stable system made up of the solid solutions which compose Portland cement, a new component is introduced which immediately results in a lock of equilibrium, which is only restored again by the liberation of free lime. The water soon becomes saturated with calcic hydrate, and the latter crystallizes out in a network of crystals which bind the particles of undecomposed cement together.

Dr. W. Michaelis, an eminent German Chemist, has done a great deal of work on the constitution of Portland cement and with the problem of the hardening of the same. His researches have been carried on during the last forty-five years and he considers that he has entirely cleared up the problem of hardening of cements. The results of his work have been translated into the English by his son Dr. W. Michaelis, Jr.,.

Michaelis' theory of the hardening of cement is not at all in accord with the crystallization theory. He attributes the hardening to the formation of colloidal

calcium hydro-silicate, and to a lesser degree also the formation of colloidal calcium hydro-aluminate and calcium hydro-ferrite. He has prepared synthetically the various hydro-silicates and hydro-aluminates and his conclusions are based upon years of experimental work.

According to this theory hydraulic cements will be more reliable and the more durable the more limited the process of crystallization during their hardening; hence hydraulic cements low in lime and alumina are the most preferable. Michaelis recommends the iron-ore cement as an ideal hydraulic cement because its calcium ferrites never crystallize and possess, if vitrified, wonderful resistance under all circumstances.

In a paper read before the Association of German Portland Cement Manufactures, on Feb. 17, 1906, Michaelis considers tri-calcium silicate as an impossible chemical combination. He recognizes tri-calcium di-aluminate and tri-calcium-di-ferrite, penti-calcium-di-aluminate and tri-calcium-aluminate.

The work of Arthur L. Day and E. S. Shepherd upon, "The Lime silica Series of Minerals", at the Carnegie Institute of Washington in 1906, is one of the most thorough and reliable works carried out along this line up to the present time, and the conclusions they arrive at are generally accepted by the investigators into the con-

stitution of these minerals.

Their methods of procedure are along the line of physical chemistry. They consider that mineral solutions are only chemical solutions over again with slightly different components and a very different range of temperatures, and pressures. They have attempted the study of mineral and rock formation by a direct application of the principles and methods of quantitative physics and chemistry, or by direct measurement of the temperatures where the minerals combine and separate like the solutions of ordinary chemistry under ordinary conditions.

They began their investigations by first determining the physical properties of the pure components, lime and silica.

Having chemically pure and well mixed preparations they secured a preliminary survey of the field in hand in the following manner. The mineral Wallastonite is known to posses a melting temperature lower than either lime or silica. There is therefore immediate reason for anticipating entectic relations somewhere in the series. If Wollastonite forms a entectic with components on one or both sides of it, mixtures containing slightly more lime or slightly more silica will have lower melting temperatures than it. A simple and effective mode of procedure is therefore to take a tiny pinch of a number of the

percentage mixtures adjacent to Wollastonite, place them in order upon a narrow platinum ribbon which can be heated electrically to uniform brightness and observe the order in which they melt. If a entectic is present on either side of the compound, it will be the first to melt and the compound last.

Proceeding in this way the investigators were able to locate three entectics corresponding to 37, 54 and 67.5 per cent CaO and two compounds corresponding to 48 and 65 per cent CaO. Practically all the compositions from pure lime to pure silica at intervals of 1 or 2.5 per cent and all temperatures from 500° C to 2100° C were included in this test.

The investigators conclude from this preliminary investigations that they have located two compounds the metasilicate and the orthosilicate, and missed two which might have been expected, the compound $3SiO_2.4CaO$, and tri-calcium silicate. Their next step was to bring all resources to bear and to see if these two supposed compounds really exist.

The compound $3\ SiO_2.4CaO$ was first taken up. A large charge of this particular composition was repeatedly melted and examined under the microscope but it failed to show homogeneous structure or any characteristic property of a compound. The melting temperatures of these

mixtures were within direct control so that the temperatures could be held constant at any desired point, and then by rapid cooling (quenching in mercury) to fix any phase which might have been present and become unstable below that temperature. Here again it was found that pseudo-wollastonite and the calcium orthosilicate were the only phases which could be separated from this or any mixture of the pure components in the neighborhood. From this the investigators conclude that the compound $3CaO_2$. $4CaO$ cannot exist.

In an exactly similar manner the tri-calcium silicate was taken up. The components were fused together in the proper proportions and the product examined under the microscope. In every case the product was found to consist of the orthosilicate and free lime. Most previous investigators appear to have depended for microscopic evidence upon the ordinary optical figures and interference colors. It so happens that this mixture when fused crystallizes in an extremely fine structure in which the interference colors are quite different from those of the orthosilicate to be sure, but this is the result of the fine state of division and the overlaping of the crystals and not to another compound. The tri-calcium silicate prepared and described by Clifford Richardson was examined and found to be a mixture of the orthosilicate and free

lime. Many other tri-calcium silicates prepared by others were examined with always the same result. From these investigations the investigators conclude that tri-calcium silicate cannot exist.

The work on "The Binary Systems of Alumina with Silica, Lime and Magnesia", carried on at the Carnegie Institute of Washington by Shepherd, Rankin and Wright is a very valuable work and the most thorough of its kind. In their conclusions they state that there are four definite compounds of lime with alumina, namely $Al_2O_3.3CaO$: $3Al_2O_3.5CaO$: $Al_2O_3.CaO$ and $5Al_2O_3.3CaO$. They say that of these aluminates it seems probably that only $Al_2O_3.3CaO$ will occur in Portland cement.

This seems to be the gist of all the available literature on this subject up to the present time. It will be noticed that the earlier investigators were repeatedly at variance upon points that seem clear to us now, and it does not seem that they had sufficient grounds to base their conclusions upon. The later investigators are more in unison upon the various problems in question, and their conclusions are drawn inthe light of years of experimental work. I do not wish to place too small a value upon the earlier investigators' work because it is because of this preliminary work that the men that followed were able to look upon the subject from a broader view-point.

Free Lime in Portland Cement:

In the previous part of this paper we have shown that lime may be present in portland cement in combination with silica, iron oxide, or alumina; that the clinker is capable of forming solid solutions with Fe_2O_3. It has been maintained that a part of the lime may be present as a solid solution of lime in the various silicates, ferrite and aluminates present in portland cement. It is possible though somewhat improbable, that the lime may be present in the clinker and yet not be in combination or in solid solution. This lime we call "free lime", while we designate as "uncombined" lime that lime present both as free lime and in solid solution.

It is evident from a study of the work which has been done on the determination of the constitution of cement that the highest compounds which lime forms with silica, ferric oxide and alumina in portland cement are as follows: - di-calcium silicate, $2CaO.SiO_2$, tri-calcium ferrite, $3CaO.Fe_2O_3$, and tri-calcium aluminate, $3CaO.Al_2O_3$. The magnesium is probably present as magnesium silicate, $MgO.SiO_2$. The sulfuric anhydride is present as gypsum,

$CaSO_4$, in which form it was added to the cement. Given the analysis of a cement one can by a simple method of calculation demonstrate that there is present considerable "uncombined" lime. As examples of this method, let us take the following analysis of typical cements. Eckel.

	I	II	III.
SiO_2	20.54	22.25	24.24
Al_2O_3	8.55	7.65	7.26
Fe_2O_3	3.84	3.35	2.54
CaO	63.85	62.85	64.96
MgO	.66	.78	2.26
SO_3		1.34	.41

Let us consider first, the analysis of cement II. We have assumed that MgO is present as $MgO.SiO_2$, so that the .78 parts of MgO are combined with 1.17 parts SiO_2. This amount of silica subtracted from the total (22.25 parts) leaves behind 21.08 parts SiO_2, to combine with the lime. In order to form $2CaO.SiO_2$, the 21.08 parts of SiO_2 will require 32.68 parts of CaO. To form $3CaO.Al_2O_3$, the 7.65 parts of alumina require 11.60 parts CaO. To form $3CaO.Fe_2O_3$ 3.52 parts of lime are required to combine with the 3.35 parts of Fe_2O_3. The 1.34 parts of SO_3 require .94 parts of CaO to form $CaSO_4$. Or, in all

a total of 48.74 parts of CaO are required to form the most basic compounds which investigators have decided are present in portland cement. But this cement contained 62.85 parts of lime. There remains, therefore, 14.11 parts of "uncombined" lime. A similar calculation for I and III, yields 10.95 and 11.83 parts respectively of uncombined lime. This method has been applied to large numbers of cement analyses, and in every case the presence of uncombined lime has been demonstrated.

One observes that, in making the above calculations, it was assumed that only those compounds with silica ferric oxide and alumina which require the highest percentage of lime were present. Had the presence of compounds of silica, ferric oxide and alumina with smaller proportions of lime than those previously described been admitted, the amount of uncombined lime in the cement would have been materially increased. It is also to be observed that no attention has been given to the presence of such complex compounds as might be formed by ferric oxide, alumina and silica because there is no general agreement among investigators on the presence of such complex substances in clinker. What fraction of this uncombined lime is present as a solid solution of lime in the various silicates, aluminates, and ferrites of cement, is a very difficult matter to determine. Many attempts have been made at dif-

ferent times to detect free lime in cement. A short resume of the work done on the subject follows.

Tests for Free Lime in Portland Cement.

Professor Alfred H. White of the University of Michigan has worked out a microscopic test for free lime in Portland cement. This test is based on the formation on the slide of the microscope of a characteristic cyrstalline calcium phenolate readily recognizable in polarized light. The reagent is prepared by dissolving crystallized phenol in an immiscible and rather non-volatile solvent and adding a trace of water.

The reagent preferred by White consisted of 5 grams of phenol dissolved in 5 c.c. of nitrobenzol with two drops of water added to this solution.

In making this test about two or three milligrams of the finely powdered material are placed in the center of the microscopic slide, a drop of the reagent put upon it then a cover glass. When the freshly prepared slide is put under the microscope the lime being isotropic is almost invisible and the whole field is dark. Within a few minutes the edges of the fragments of lime begin to show brilliant points which in a quarter of an hour develop into brilliant clusters of radiating needles. Very little further change is noticeable in six hours but in twenty-four hours the reagent will have evaporated and the crys-

tals disappeared.

No substance other than CaO or $Ca(OH)_2$ has been found to give this reaction. White says that with one exception his attempts to make a tri-calcium silicate that would not show free lime have been failures.

White explains that the test in cement mills is commendable for with the boiling test as his only reliance the cement chemist must always work twenty-four hours behind his rotaries. The test is so simple that it can be made, if desired by the burner who can thus control his product hour by hour.

One may observe that the presence of water is essential to successfully carry out the above tests. It is a matter of common knowledge that water acts very strongly on portland cement causing the setting free of lime. That the crystals of calcium phenolate are due to the presence of free lime in the cement or are a result of the action of the lime formed by the decomposition of the cement by water, is a matter of doubt.

Another test proposed by R. Bradenburg detects the free lime and determines it quantitatively. In this test a solution of ammonium bromide in absolute alcohol is distilled in the presence of the cement to be tested, the ammonia evolved being regarded as a measure of the free lime in the cement. The alcohol must be absolute. It has

been found that the ammonium bromide is not decomposed by boiling with its alcoholic solution either alone or in the presence of calcium carbonate. The chemical reactions taking place are according to the following equations;

$$2NH_4Br + CaO = 2NH_3 + H_2O + CaBr_2$$

and

$$NH_3 + H_2O = NH_4OH.$$

This method is said to be accurate up to one tenth of one per cent CaO.

In his paper on Vyrnivy dam of the Liverpool Waterworks, Mr. Deacon advocates the observation of the rise of temperature during setting as a test for free lime. A hand sample of cement, a small vessel of water, a beaker and a thermometer are left together for a short time to acquire a uniform temperature. The cement is gauged into the beaker as quickly as possible with just sufficient water to render it plastic and the thermometer immediately being pressed into it, the initial temperature is recorded. If within fifteen minutes the rise of temperature exceeds 2° F, or within sixty minutes 3° F the cement should be further exposed before use.

Mr. D. B. Butler seems to have proved that the rise in temperature is rather due to the chemical action of crystallization than to the presence of free lime. With slow setting cements the crystallization is of course slow and therefore the rise in temperature in a short time

would not be appreciable. In this case the above test may show the presence of free lime.

Another proposed test depends on the fact that calcium hydroxide loses its water of constitution at 450° to 480° c., while the other constitutents of set Portland cement lose their water of hydration at 160° C. In this test a sample of cement is heated for two or three hours at 180° - 200° C. In another sample carbon dioxide is determined and in another loss on ignition. Upon deducing carbon dioxide and loss on heating to 200° C from the total loss on ignition, we arrive at the amount of water in the calcium hydroxide present, and hence, at the CaO.

Experimental Work.

The cement used in my experimental work was manufactured by the Ash Grove Lime and Portland Cement Co., of Chanute, Kansas,. The analysis given by the Ash Grove Chemist follows:

SiO_2, 23.20: Al_2O_3, 8.10: Fe_2O_3, 2.71: MgO, 1.00 SO_3, 1.20: CaO, 63.50. Total 100.71.

On the basis of the calculation for uncombined lime given in a previous part of this paper, this cement contains ? per cent of "uncombined"lime.

I next took up White's microscopic test for free lime and studied it more closely in order to find its defects or virtues. I tried to answer the following ques-

tions in this respect:

1. Are there $Ca(OH)_2$ crystals formed during this test that would interfere with the detection of the phenolate crystals?

2. Are the crystals formed really calcium phenolate crystals or pure phenol crystals.

3. Do different solvents have any marked effects?

4. Is it necessary to add any water at all to the reagent in order to produce the crystals?

5. What percentage of lime may be readily detected?

Besides ordinary cement that passes a 200 mesh sieve I used cement that is twenty times as fine as the former. This cement is completely decomposed by water in ten minutes while three months is required to decompose ordinary cement. The fine cement therefore decomposed about 13000 times as quickly as the ordinary cement. This fine cement ought to react quickly with the various reagents for testing for free lime and thus afford some interesting experiments.

I first made up a couple of microscopic slides using pure $Ca(OH)_2$ and CaO. On these slides I could easily detect the long slender crystals of calcium phenolate that White describes. From these slides I became familiar with the crystals so that I could recognize them when I saw them.

In order to answer the first question I made up the following slides to be examined under the polarizing microscope.

(a) A few milligrams of ordinary cement with pure water. No crystals could be detected.

(b) A few milligrams of the fine cement with pure water. No crystals could be detected.

From these tests I conclude that there are no calcium hydroxide crystals formed to interfere with the test.

In order to answer the second question I made up a slide with a drop of a solution of five grams phenol and five c.c. nitrobenzene. No crystals of any kind could be detected at any time.

The answer to the second question seems to be that there are no crystals of pure phenol formed on the slide.

To answer the third question I made up phenol solutions using the following solvents; nitrobenzene, benzene, toluene, glacial acetic acid, Xylol, ether and alcohol. These solutions each contained five grams of pure phenol and five c.c. of the solvent. I made up slides using ordinary cement with these solutions and examined them for crystals at periods of one hour, two and one-half hours and four hours. No crystals could be detected at

any time. It is hard to draw any conclusions in this case because there are no results to judge from . White recommends an immicible and rather non-volatile solvent. This would point in favor of the nitrobenzene or xylol solution.

In order to answer the fourth question I added one drop of water to 5 c.c. of the above solutions and made up slides with the resulting solutions and ordinary cement. No crystals could be detected. In the next slide I used the watered nitrobenzene solution and the fine cement. The phenolate crystals could be detected immediate ly.

Now I recall that I obtained no crystals of any kind on the slide made up of the anhydrous nitrobenzene-phenol solution and fine cement, and I have obtained very distinct calcium phenolate crystals by using the watered solution. I must conclude therefore that it is necessary to add a little water to the reagent in order to obtain any crystals at all.

To my mind the one drop of water added to the reagent in this case is sufficient to decompose the small quantity of cement used and it is hard to understand how this can be a test for "free lime" if the lime in combination is brought into solution during the process.

In answering the fifth and last question I mixed five grams of ordinary cement with .5 gram $Ca(OH)_2$ using a

few milligrams of this mixture and the water nitro-benzene solution, the phenolate crystals could be detected immediately.

From a mixture of 10 grams ordinary cement and .25 gram $Ca(OH)_2$ I could detect very few crystals at first but they became quite evident after half an hour.

From a mixture of one gram ordinary cement an .01 gram $Ca(OH)_2$, no crystals could be detected at first, after standing for half an hour there were crystals in abundance.

By the above tests I find that one per cent lime can be detected within the course of half an hour by this test.

In general I have reached the following conclusions concerning White's Microscopic test for free lime in Portland cement. It is necessary to add a small amount of water to the phenol solution in order to detect free lime at all. The crystals formed are calcium phenolate crystals and nothing else. The nitrobenzene is probably the best solvent to use for phenol. I have found that up to 2.5 % lime can be detected immediately and 1. % in the course of twenty minutes of half an hour. It is very probable that 0.5 per cent of lime could be detected if the slide were allowed to stand for an hour or an hour and a half.

half.

The crystals in question in this test are very distinct and characteristic, and I do not think could be mistaken once seen. The only weak point in the test in my judgement is in the fact that a small amount of water must be added to the reagent. This undoubtedly decomposes the cement and if this is the case the test cannot be a true one.

I am very sorry that my time is limited, and I have not time to investigate the other proposed tests for free lime.

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The solution used here was phenol dissolved in nitrobenzene plus a trace of water.

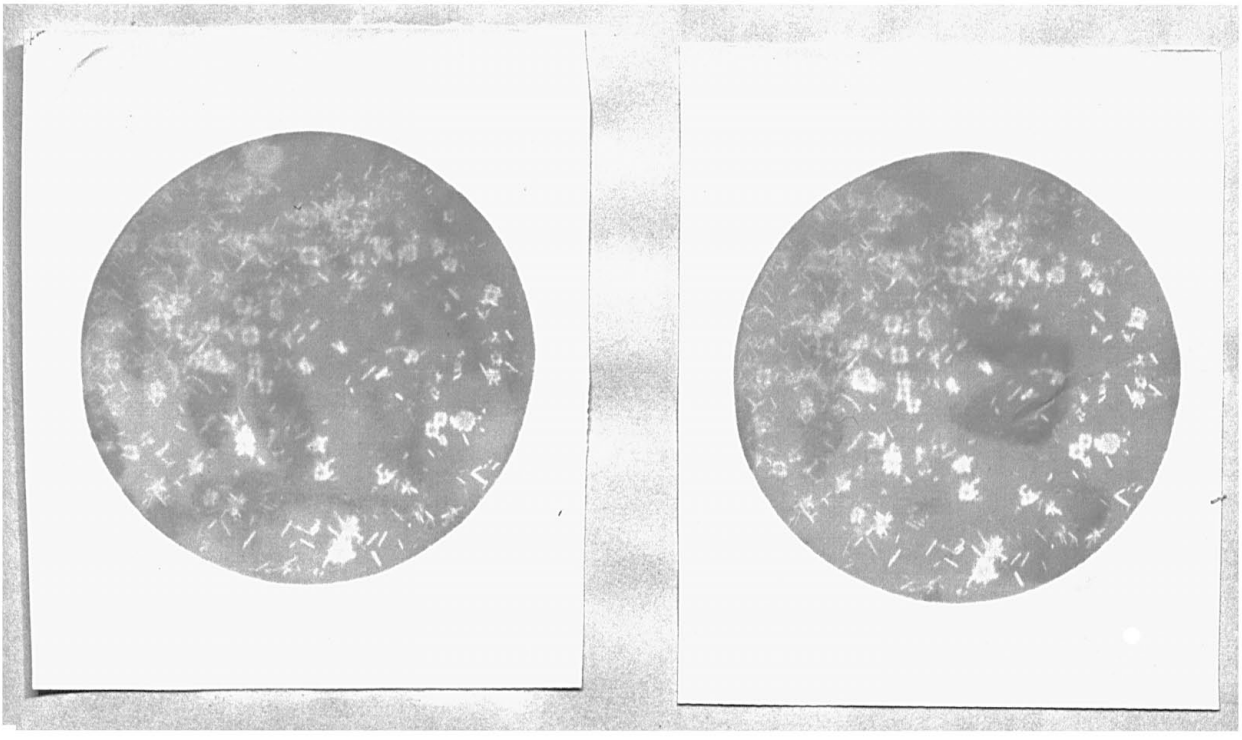

Fig. I

Fig. II.

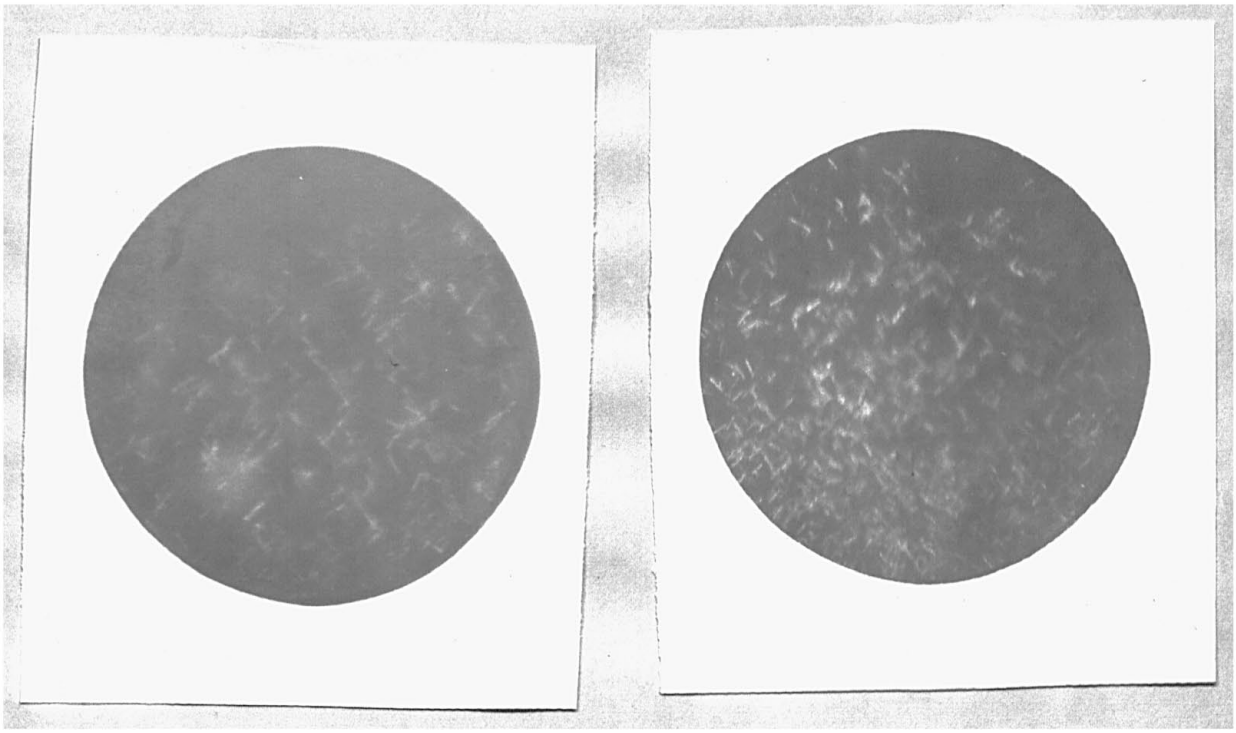

Fig. III.

Fig. IV.